

pressing step to adhere the diffusion media layers to the MEA before the fuel cells are assembled into the stack, and therefore, independent claim 15 is not obvious in view of the patents referred to above. Applicant argued that by not using the hot-pressing step prior to assembly of the fuel cell stack, the MEA was less likely to fail along the outer edge of the catalyst, as a result of the edge of the catalyst being pressed to the diffusion media layers during the hot-pressing step.

The Examiner apparently agreed with Applicant's position. However, the Examiner maintained the rejection stating that Applicant must show objective evidence with regard to the advantage of eliminating the hot-press step or the bonding step to increase the lifetime of the MEA in a fuel cell stack, citing In re Schulze, 145 USPQ 716, 718 (CCPA 1965). The relevant portion of In re Schulze is provided below.

We think appellant's contentions lack merit. While it is quite true that such limitations are found in the claims, it seems to us that a sufficient answer to the arguments may be found in appellant's specification, which makes it clear that those limitations are no more than details, culled from a specific example and lacking in patentable significance because well within the skill of the art.

For example, we do not find the expression "close to" in the claims to patentably distinguish over Ditto, which specifically discloses mixing the bitumen and water in an emulsifying mill and "using it immediately." As the solicitor points out, for aught the record shows, it is immaterial where the mixing takes place. Nor do we find anything in the record by way of disclosure or affidavit that the 200-205° F solid particle temperature is critical or is otherwise patentably distinguishable from the solids temperature of 212°F or higher disclosed by Elod, or the solids temperature of 225° F disclosed by Sommer. Argument in the brief does not take the place of evidence in the record. In re Cole, CCPA 919, 326 F.2d 769, 140 USPQ 230. What does appear important, from appellant's disclosure as well as the references, is that the solids temperature be at least 200° F to prevent cooling of the bitumen before it can spread uniformly on the particles. Indeed, appellant discloses in other portions of his specification a temperature range of 200-212°F as suitable. Finally, as noted earlier, Sommer recognizes that the temperature and pressure parameters of the process may be varied as necessary to control the coating thickness.

Applicant submits that a careful review of this section of the In re Schulze decision shows that the court took the position that the temperature range being considered as to whether it made a claim patentable was not a critical part of the invention, but merely details of a specific example. In other words, the Applicant was relying on an insignificant part of the invention, as determined by the discussion in the record, to argue that the claimed temperature range was not obvious in view of the prior art of record. Applicant submits that this is not the situation in this application because Applicant has identified ample and detailed discussion in the specification of the desirability to eliminate the hot-press step or bonding step when fabricating MEAs to increase the durability of the stack.

Paragraph 9 of the specification discusses that the known decal substrate transfer processes for fabricating MEAs exhibit failure along the catalyst edge that corresponded to the hot-pressing step. Paragraphs 10 and 11 of the specification also discuss that the MEA fails along the edge of the catalyst layer when the MEA is prepared as a catalyst-coated diffusion media (CCDM) instead of a CCM, where the CCDM process includes a hot-pressing step. Paragraph 26 of the specification talks about an MEA prepared as a CCDM MEA according to the invention without a hot-pressing step, where the MEA exhibited five times the lifetime and two orders of magnitude lower fluoride ion release rate than that of a CCM MEA and a CCDM MEA prepared with a hot-press step. The inventors know these things because they conducted specific tests using an MEA prepared by their inventive process and those of the known CCM and CCDM processes. Figure 2 of the specification shows polarization curves 40 and 42 for an MEA prepared by the process of the invention without hot-press lamination to membrane, and graph line 44 shows a polarization curve for a standard CCM MEA that does include a hot-press

lamination to membrane. Those skilled in the art would recognize that the polarization curves 40 and 42 would provide better performance and longer life of a fuel cell.

Applicant is submitting herewith a copy of the original Record of Invention document from which the instant application was prepared. This document includes another figure, figure 3, that shows fluoride release rates for MEAs prepared conventionally and by the process of the invention that does not include a hot-pressing step, as discussed in paragraph 26. This graph and the related discussion show that the fluoride release rate for the standard CCM MEA and the CCDM MEA of the invention are different, where a lower fluoride loss leads to a longer fuel cell life.

Based on the discussion above, Applicant respectfully submits that the evidence in the record is sufficient to show that eliminating the hot-press step or bonding step to fabricate an MEA provides a longer fuel cell stack life, and that further objective evidence is not necessary.

It is now believed that this application is in condition for allowance. If the Examiner believes that personal contact with Applicant's representative would expedite prosecution of this application, she is invited to call the undersigned at her convenience.

Respectfully submitted,

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RECORD OF INVENTION

This Record of Invention must be completed with sufficient detail so that your invention can be understood and evaluated by both your engineering management and by a GM Legal Staff patent attorney. Novelty and competitive significance of your invention will be evaluated based on the information you provide.

Invention Title: A Durable Membrane Electrode Assembly – Catalyst Coated Diffusion Media with no Lamination to Membrane

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* If there are more than two (2) inventors for this invention use the template at the end of this form.

Answer questions 1 - 8, completing all of them to the best of your knowledge.

1. This invention was first thought of on: 12/02
2. This invention has been or is expected to be disclosed outside GM on: no
3. This invention has been used or is committed to be used in production on: no
4. This invention has been offered for sale outside GM on: no
5. Was this invention made while working on a Government Contract? ☐ Yes ☒ No

If yes, identify the government Contract No. _____

6. Identify the product or process in which the invention is incorporated: MEA fabrication
7. List all individuals who can provide information about the making of the invention. This list may include individuals who made the first sketch, description, or tests and individuals who are familiar with the facts relating to the making of the invention.
Hubert Gasteiger (GM/FCA), Brian Litteer (GM/FCA)

8. Each inventor has a legal duty to disclose all information known that is material to patentability of this invention. Such information includes the relevant prior art, which may be in the form of current or past products, equipment, processes, materials, patents, publications, advertisements, displays, and unpublished developments and proposals—whether originated by you, others in GM, competitors, suppliers, customers or others. Such information also includes disclosure of this invention outside GM, sales and offers of products using this invention, use of this invention in production and disputes about who should be considered as an inventor of this invention. To comply with the duty to disclose, list here and attach a copy of all such information, to the extent known.

Sompalli, B., Gasteiger, H., Mathias, M., Scozzafava, M., *Methods of Preparing Membrane Electrode*, US 6,524,736, 2003.

Yan, S.G., Scozzafava, M., Wang, Z., *Method for MEA Fabrication – Nonporous Decal Transfer of Catalyst*, GM-FCA Patent Application: GP-302 911, 2002.

Hards, G. A., Ralph, T.R., *Process for the Preparation of electrode Assemblies*, EP 0 577 291 B1, 1998.

Answer question 9 thoroughly.

9. Describe the invention in sufficient detail so that its nature, operation and usefulness can be understood. (Attach drawings, diagrams and further description, when necessary. Additional guidelines are listed below.)

The optimization of polymer electrolyte fuel cells is essential for viable applications. Membrane electrode assemblies (MEAs) for polymer electrolyte fuel cells comprise of a polymer electrolyte proton conducting membrane, anode and cathode catalyst layers and anode and cathode diffusion media. In order to achieve low cost, efficient, and durable fuel cells, the fabrication process of the MEA needs to be improved. This disclosure describes a method to fabricate MEAs that is not only simplified from previous methods but also affords increased durability.

Membrane electrode assemblies (MEAs) for polymer electrolyte fuel cells comprise of a polymer electrolyte proton conducting membrane, anode and cathode catalyst layers and anode and cathode diffusion media. The catalyst layer may be coated on the diffusion media or on the membrane. In the latter case, the catalyst may be applied directly on the polymer membrane or indirectly by coating the catalyst onto a decal substrate, then transferring onto the membrane via a hot-pressing step. This type of MEA is hereby called catalyst coated membrane (CCM). The decal transfer method has been reported in prior art where the substrate is a teflon blank [1,2]. A recent GM patent discloses a decal transfer by coating the catalyst onto a porous expanded PTFE (polytetrafluoroethylene) (ePTFE) substrate resulting in an improved MEA [3]. However, this expanded PTFE is expensive and not re-usable. Upon transfer (peel off decal, leaving catalyst on polymer electrolyte membrane), some amount of the catalyst or catalyst ink components remain on the ePTFE. The ePTFE also stretches, deforms, and absorbs solvents making a cleaning step very difficult. Hence, every piece of ePTFE used to make each anode and each cathode layer is discarded.

In another recent disclosure, a non-porous ethylene tetrafluoroethylene (ETFE) decal substrate was used in place of the porous ePTFE [4]. In this case, the MEA fabrication process was the same except there is minimal loss of catalyst and ionomer on the substrate. Virtually all of the coating is decal transferred. The substrate does not deform and can be re-used. In both cases, the anode and cathode decals are cut to the dimensions of the final electrode size, then hot pressed to the perfluorinated membrane, and subsequently, the decal substrate is peeled off.

MEAs prepared with both types of decal substrates have exhibited failure along the catalyst edge. This corresponds exactly to the edge of the decal during hotpressing. Since the decals are discrete in size and have a thickness around 3mils, during hotpressing, the decal or active area section of the membrane would experience higher pressures than the remaining bare membrane. This translates to possible weakening of the perfluorinated membrane along the catalyst edges.

Other prior art describes MEAs prepared as catalyst coated diffusion media (CCDM) instead of CCMs [5]. The diffusion media is typically a carbon paper substrate that is coated with a microporous layer. The microporous layer is a coating comprised of a mixture of carbon and teflon. The catalyst ink is then typically patch coated via screenprinting on top of the microporous layer and then compressed. To prepare the final MEA, a piece of bare perfluorinated membrane is sandwiched in between two pieces of CCDM with the catalyst sides facing the membrane and then hot pressed to bond the CCDM to the membrane.

In this disclosure, MEAs are also prepared as CCDMs in which the diffusion media media is typically a carbon paper substrate substrate that is either coated with teflon or coated with a microporous layer. The catalyst ink is then applied on top of the teflon or microporous layer coating the entire surface. Additionally, a thin ionomer layer is sprayed on top of the catalyst. The ionomer spray solution is a mixture of ionomer and methanol. To prepare the final MEA, a piece of bare perfluorinated membrane is sandwiched in between two pieces of CCDM with the catalyst sides facing the membrane. There is no additional hot pressing or processing. Figure 1 shows the structure and components of the disclosed catalyst coated diffusion media MEA.

The ionomer overspray layer is crucial for good ionomeric contact between the CCDM and the membrane when there is no hotpressing. Figure 2 is a plot of polarization curves comparing performance of a CCDM with ionomer overspray and without overspray with that of a CCM MEA prepared via ePTFE decal transfer. During fuel cell operation, at typical temperatures around 80C, the catalyst and microporous layer will completely transfer onto the membrane, rendering essentially a CCM MEA.

This present method has distinct advantages in many respects:

1. By having no decal transfer or hotpressing, the initial membrane does not get prematurely weakened along the catalyst edges, leading to enhanced durability.
2. Having the catalyst coated over the entire DM surface has proven to be better than having catalyst coated as a patch in the DM. It has been seen that in the latter case MEAs also have membrane damage at the catalyst edge (also failure mode observed for a CCM). The CCDM MEA, where the catalyst was coated entirely out to the edge of the DM exhibited mechanical failure of the membrane outside of the DM.

MEAs prepared as CCDMs exhibited 5 times the lifetime and 2 orders of magnitude lower fluoride ion release rate than that of CCMs as well as CCMs. MEAs prepared with a hot pressing step provide the degradation of MEA performance due to testing at 95°C and partially dry conditions at 300 kPa (abs).

A standard CCM MEA tested in the 50cm² platform, lasted 65 hours before developing severe failures along the catalyst layer edges. The MEA degradation is usually monitored by Fluoride elution in the product water. For the standard CCM MEA tested, F⁻ loss was 7x10⁻⁷g/cm²/hr. Under similar circumstances, an MEA with Catalyst-coated diffusion media architecture had a much lower F⁻ loss of 5x10⁻⁹g/cm²/hr, with a longer lifetime of 350 hours. Short stacks run under similar conditions had similar lifetimes and fluoride release rates.

It is our understanding that bare membrane exposure to reactant gases, leads not only to severe mechanical problems (such as shorting of membranes), but also to increased oxygen crossover from cathode to anode. Hydrogen peroxide suspected to form on the anode side due to such crossover, attacks the ionomer in the membrane and electrode leading to severe chemical degradation of the MEA. Coating the DM entirely with catalyst layer eliminates any bare membrane exposure, cutting down peroxide formation, thus curtailing chemical degradation, as is evident from the Fluoride loss in Figure 3.

References:

1. Wilson, M.S, Gottesfeld, S., *Thin-film catalyst layers for polymer electrolyte fuel cell electrodes*, Journal of Applied Electrochemistry, **22**, 1992, 1-7.
2. Wilson, M.S., *Membrane Catalyst Layer For Fuel Cells*, USPN 5234777, 1993.
3. Sompalli, B., Gasteiger, H., Mathias, M., Scozzafava, M., *Methods of Preparing Membrane Electrode*, US 6,524,736, 2003.
4. Yan, S.G., Scozzafava, M., Wang, Z, *Method for MEA Fabrication – Nonporous Decal Transfer of Catalyst*, GM-FCA Patent Application: GP-302 911, 2002.
5. Hards, G. A., Ralph, T.R., *Process for the Preparation of electrode Assemblies*, EP 0 577 291 B1, 1998.

Mechanical and Electrical Devices: Include illustrations assigning reference numbers to the main elements and refer to the reference numbers in a description that explains how the main elements are connected or related and how they operate.

Electrical Circuits and Controls: Include circuit diagrams and a functional description.


Computer Software and Manufacturing or Business Processes: Include a flowchart or other step-by step overview.

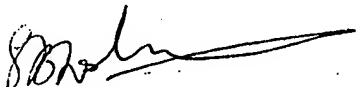
Chemical Inventions: Identify all essential materials used, and alternatives therefor, in chemical terms – not tradenames. Identify and quantify all significant variables (e.g. temperature, pressure, concentration, pH etc.) of the process or material

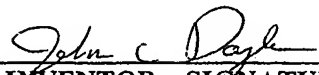
specifying operating ranges and
one working example of the

preferred example. Discuss the significance of each variable. Provide a recipe for at least
one.

I hereby assign this invention to General Motors Corporation
and authorize General Motors Corporation to file an application on my behalf.


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Answer the following questions if helpful in describing this Invention

10. What benefits will be realized by using this invention?

1. *The present invention will afford alternatives to the GPC MEA fabrication process such that cost will be significantly decreased*
2. *The coating procedure is exceedingly simple, and no wastage of coating inks or costly substrates.*
3. *The hot-pressing step is eliminated, which is a source of uncertainty due to uncontrolled pressure/temperature fluctuations.*
4. *MEA durability is significantly improved*

11. What is the state of development of this invention?

Small scale and stack-size MEAs have been demonstrated. The catalyst coated diffusion media with no lamination to membrane has shown 5x improved lifetimes compared to standard catalyst coated membrane MEAs.

12. To the extent known, what alternatives exist for accomplishing substantially the same result as this invention?

MEA fabrication by coating catalyst on diffusion media with no subsequent hot pressing or ionomer overspray on top of the catalyst to date has not been disclosed.

13. Describe the background of the invention. This description may include the state of the prior art and may identify deficiencies in the prior art that are overcome by this invention.

MEA fabrication by coating catalyst on diffusion media is widely known. However, this process requires hot pressing or laminating of the perfluorinated membrane to the diffusion media. There is no ionomer overspray layer so the only way to have good ionomer contact of the catalyst to the membrane is by hot pressing. MEAs prepared this way have shown that premature failures still occur along the catalyst edge suggesting that hot pressing has weakened the membrane. This invention includes an ionomer overspray layer which during fuel cell operation will allow the catalyst to bond to the membrane. This invention allows for no hot pressing or pre-lamination of membrane in any way. This way, the membrane has not undergone any premature weakening by MEA processing.

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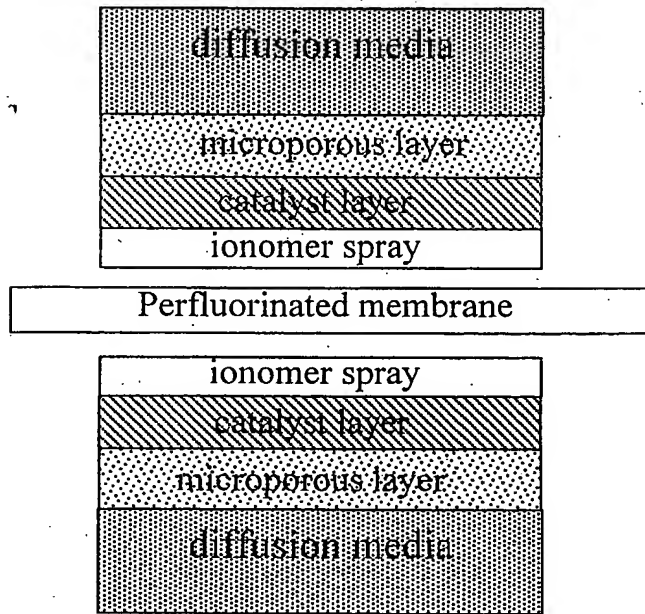


Figure 1. Structure of MEA of catalyst coated diffusion media.

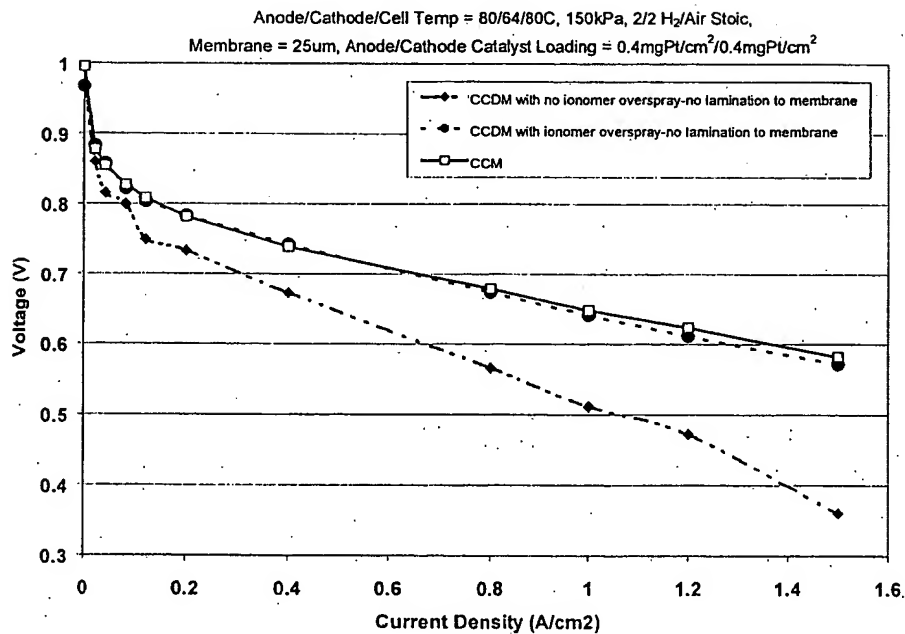
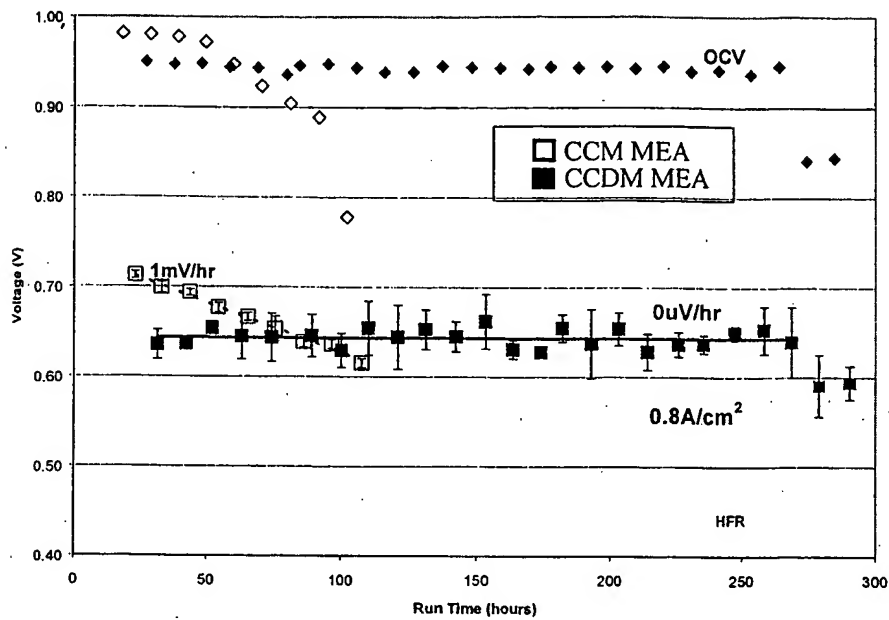


Figure 2. Polarization curves comparing CCDM with and without ionomer overspray with no lamination to membrane vs. standard CCM MEA.



CCM: F⁻ release $\sim 7 \times 10^{-7}$ g/cm²/hr
 CCDM: F⁻ release $\sim 5 \times 10^{-9}$ g/cm²/hr

Figure 3: Small-scale (50cm²) durability data at 95 °C, 300 kPa(abs), 75/50%RH, 2/2 stoich, H₂/Air. CCM vs. CCDM. 1mil membrane ionomer in electrodes, 0.4mg_{Pt}/cm²-per-side